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FISSION PRODUCT RATIOS OF THE PUREX FILTER

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FISSION PRODUCT RATIOS OF THE PUREX FILTER

INTRODUCTION

Measurements of fission product ratios were made on various samples of the Purex canyon exhaust filter to determine the manner and time interval in which the filter became plugged with foreign material. Results for samples from different levels within the filter bed were compared to investigate accumulation as a function of depth.

SUMMARY

Strontium-89/strontium-90, Zr-95/Cs-137, Ru-103/Ru-106, and Ce-141/Ce, Pr-144 ratios were determined. These were compared to a constant rate model for accumulation of fission products on the filter. Observed Sr-89/Sr-90 and Zr-95/Cs-137 ratios fall within a range of values typical of normal plant operation, specifically long-term accumulation of Hanford material irradiated at 10 MW/T to between 600 and 900 MWD/T total exposure and cooled between 120 and 200 days. Low Ru-103/Ru-106 and Ce-141/Ce, Pr-144 ratios definitely rule out rapid accumulation of short-cooled material as the build-up mechanism but are not sensitive indicators in the case of long-cooled material.

Ratios did not vary significantly with sample location, indicating that accumulation age does not differ with depth within the filter.

EXPERIMENTAL AND DISCUSSION

I. Sampling

The half inch diameter core sample from bay one and the four inch diameter, twenty-three inch long core sample from bay three were analyzed. The appearance of the core materials and the sampling techniques employed are discussed in (1). Sample designations and brief descriptions of source and nature are summarized in Table I.

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TABLE I

SAMPLE SUMMARY

<u>Designation</u>	<u>Source and Description</u>
1/2" Core, Bay 1, Received 4/13/64	
Gray Salt	0.1720 g gray crust dissolved by heating with conc. HCl.
White Salt	0.4257g white crust dissolved in water.
4" Core, Bay 3, Received 4/27/64	
H ₂ O-1	Water leach of loose 3" end plus 3-1/2" of core (section 1) 7.0g salt dissolved.
HCl-1	Subsequent 6N HCl leach of section 1 1.8g salt dissolved.
H ₂ O-2	Water leach of adjacent 5-1/2" of core (section 2) 4.9g salt dissolved.
HCl-2	Subsequent 6N HCl leach of section 2 2.3g salt dissolved.
H ₂ O-3	Water leach of adjacent 5-1/2" of core (section 3) 8.4g salt dissolved
HCl-3	Subsequent 6N HCl leach of section 3 0.7g salt dissolved.
H ₂ O-4	Water leach of 5-1/2" crusted end of core (section 4) 27.7g salt dissolved
HCl-4	Subsequent 6N HCl leach of section 4 9.7g salt dissolved.
Leached #4 Wool	Subsequent to leaching, 0.1512g section 4 glass wool dissolved in HF-HCl-alcohol
Section #4 Crust	35.2 mg of loose crust (prior to leaching) dissolved in aqua regia.

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Isotopic analyses were performed on secondary 1N hydrochloric acid dilutions of the primary solutions of Delvin, et al⁽¹⁾, except in the case of "leached #4 wool" and "section #4 crust". For the former, a secondary 1N hydrochloric acid dilution was prepared from a slightly turbid hydrofluoric acid - hydrochloric acid - alcohol special dissolution of the leached wool. In the case of the latter, a special aqua regia dissolution was analyzed directly.

A mixed fission product radioisotopic standard was prepared for analysis to assist in evaluation of the accuracy and limitations of the analytical procedures.

II. Analytical

Direct gamma energy analysis of the samples showed only longer lived fission products. Chemical separations were performed for all identified isotopes to permit measurement of those not adequately resolved by direct counting. A summary of analytical and counting techniques is presented in Table II. Experimentally determined isotopic ratios are tabulated in Table III. The complete analytical data are attached as Appendix A.

The radioisotopic standard was processed simultaneously with the Purex filter samples. Measurements obtained with the separations procedures and optimum counting techniques are tabulated with direct γ -energy analysis data in Table IV. Limitations of the analytical procedures and the accuracy of the measured isotopic ratios can be estimated from recovery data of the table.

Table III reveals no significant difference or trend in isotopic ratios as a function of sampling location within the filter or its crust deposit. It is concluded that fission product accumulation is not age stratified and sequential build-up is not the mechanism.

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TABLE II

SUMMARY OF ANALYTICAL AND COUNTING TECHNIQUES

<u>Element</u>	<u>Analytical Procedure</u>	<u>Counting Technique</u>	<u>Remarks</u>
γ -emitters	Direct count	γ -energy analysis	Accuracy decreases with energy of principle gamma. Ce-141/Ce, Pr-144 and Zr-95/Nb-95 not resolved. Calculated by matrix solution of γ -spectrum.
Strontium	Gravimetric separation as the carbonate, decay, Y-90 separation	Proportional β counting, β decay	Accurate when Sr-89/Sr-90 ratio is high.
Ruthenium	Distillation as the volatile tetraoxide, gravimetric as the metal	Proportional β counting with absorbers or γ -energy analysis	β : accurate only if Ru-103/Ru-106 > 0.45 disintegration ratio. γ : somewhat better accuracy below 0.45 disintegration ratio
Cerium	HDEHP extraction, gravimetric as the oxide	Proportional β counting with absorbers	Precision poor. Ce-141 not detectable by γ -energy analysis
Cesium	Tetraphenylborate extraction, carrier free	γ -energy analysis	Low salt concentration prerequisite to quantitative extraction. Matrix corrected for small amounts of entrained Ru
Zirconium	Gravimetric separation as barium fluorozirconate	γ -energy analysis	Decontamination from Nb good. Chemical yield <75%. Precision relatively poor.

TABLE III

MEASURED ISOTOPIC RATIOS FOR PUREX FILTER SAMPLES

Sample	<u>Ru-103/Ru-106</u> <u>Direct γ Count</u>	<u>Ru-103/Ru-106</u> <u>γ Counting</u>	<u>Sr-89/Sr-90</u> <u>β Counting</u>	<u>Ce-141/Ce,Pr-144</u> <u>β Absorber Counting</u>	<u>Zr-95/Cs-137</u> <u>γ Counting</u>
1/2" Core, Bay 1					
Gray Salt	0.196	0.196	0.242	--	0.75
White Salt	0.260	0.344	0.589 ^(a)	--	0.11 ^(a)
4" Core, Bay 3					
H ₂ O-1	0.139	0.251	0.374	0.055	--
HCl-1	0.153	0.290	0.371	0.040	--
H ₂ O-2	0.163	--	--	--	--
HCl-2	0.195	--	--	--	--
H ₂ O-3	0.188	--	--	--	--
HCl-3	0.195	--	--	--	--
H ₂ O-4	0.192	0.394	0.328	0.038	] 1.93
HCl-4	0.225	0.332	0.161 ^(a)	0.004	
Leached #4 Wool	0.171	0.302	0.079 ^(a)	0.045	
Section #4 Crust	0.165	0.337	0.387	0.081	[2.19 2.20
Average Experimental Ratio	0.38 >R >0.14		0.34	<0.05	1.77

(a) Outlying values not included in calculation of average experimental ratio.

TABLE IV

ANALYTICAL DETERMINATION OF A MIXED FISSION PRODUCT STANDARD

Isotope	Standard Value $\mu\text{c/ml}$	Measured Value $\mu\text{c/ml}$	% Recovery	True Ratio	Measured Ratio
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Chemical Separations Procedures with Optimum Counting Techniques

Sr-89	1.60×10^{-3}	1.63×10^{-3}	101.8	1.33	1.39
Sr-90	1.20×10^{-3}	1.17×10^{-3}	97.5		
Ru-103	3.64×10^{-3}	3.91×10^{-3}	107.4	0.372	0.482
Ru-106	9.77×10^{-3}	8.11×10^{-3}	83.0		
Ce-141	1.15×10^{-3}	1.59×10^{-3}	138.3	0.065	0.103
Ce,Pr-144	1.76×10^{-2}	1.54×10^{-2}	87.5		
Zr-95	5.90×10^{-4}	6.03×10^{-4}	102.2	0.333	0.288
Cs-137	1.77×10^{-3}	2.09×10^{-3}	118.1		

Direct Count by γ -Energy Analysis, Calculated by Matrix Solution of the Spectrum

Ru-103	3.64×10^{-3}	3.20×10^{-3}	87.8	0.372	0.320
Ru-106	9.77×10^{-3}	1.00×10^{-2}	102.4		
Ce-141	1.15×10^{-3}	not resolved	--	0.065	--
Ce,Pr-144	1.76×10^{-2}	2.36×10^{-2}	134.0		
Zr-95	5.90×10^{-4}	6.28×10^{-4}	106.4	0.333	0.309
Cs-137	1.77×10^{-3}	2.03×10^{-3}	114.8		

III. Estimation of Build-up Duration from Isotopic Ratio Measurements

At least two build-up mechanisms may be used in interpreting Purex exhaust filter data. Isotopic ratio measurements permit estimations of accumulation interval from either formulation. The first is a "sudden build-up" model and requires the filter deposits originate from a unique batch of irradiated fuel such that isotopic ratios will be a function of only age or cooling of the material. The second, a "constant rate build-up" model, stipulates uniform accumulation over a considerable interval of time from different batches of material with similar irradiation and cooling history and permits estimation of the duration of the build-up from ratio data. Development of the "constant rate" model is included as Appendix B. Averaged isotopic ratios for the filter samples are tabulated relative to "constant rate" models for Purex feed parameter extremes in Table V.

Comparison of average Sr-89/Sr-90 ratios for Purex filters with the "constant rate" model indicates experimental measurements lie within Purex feed parameters for a 3000 day accumulation. Zirconium-95/cesium-137 ratios similarly indicate at least a 1400 day build-up. Analytical considerations make the strontium ratio probably the more accurate measurement. Ruthenium and cerium ratios are able to conform with both estimates because they are relatively insensitive indices at accumulation times of this magnitude.

The anomalous strontium ratio measurement for the bay 1 filter "white salt" sample can not be explained. The low Zr-95/Cs-137 ratio of this sample is probably due to preferential cesium solubility in water dissolutions.

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TABLE V

COMPARISON OF PUREX FILTER ISOTOPIC RATIOS WITH THE CONSTANT RATE MODEL

<u>Isotope Pair</u>	<u>Constant Rate Model, 10 MW/T 600 MWD/T, 120 Day Cooled</u>		<u>Average Ratio For Purex Filter</u>	<u>Constant Rate Model, 10 MW/T 900 MWD/T, 200 Day Cooled</u>	
	<u>1400 Day Build-Up</u>	<u>3000 Day Build-Up</u>		<u>1400 Day Build-Up</u>	<u>3000 Day Build-Up</u>
Sr-89/Sr-90	1.18	0.58	0.34	0.331	0.16
Zr-95/Cs-137	2.42	1.18	1.77	0.89	0.44
Ru-103/Ru-106	0.45	0.42	0.38>R >0.14	0.095	0.088
Ce-141/Ce,Pr-144	0.036	0.035	<0.05	0.0063	0.0063

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- (4) B. F. Judson, J. B. Kendall. Private Communication. April, 1964.

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APPENDIX AANALYTICAL RESULTSTABLE A-IANALYTICAL RESULTS FOR THE 1/2" CORE SAMPLE

<u>Measurement</u>	<u>Samples (a)</u>	
	<u>Gray Salt</u> <u>µc/g dissolved salt</u>	<u>White Salt</u> <u>µc/g dissolved salt</u>
<u>Direct γ Energy Analysis</u>		
Ru-103	96	26
Ru-106	490	100
Ce-141	Not detectable	Not detectable
Ce,Pr-144	840	400
Zr-95 ^(b)	42	5
Cs-137	56	49
<u>Ruthenium Separation</u> <u>γ Counting</u>		
Ru-103	96	28
Ru-106	490	82
<u>Strontium Separation</u>		
Sr-89	17	20
Sr-90	71	34
<u>Cesium Separation</u>		
Cs-137	61	51

(a) Sample received 4/13/64. Analytical results corrected for radioactive decay to 4-16-64.

(b) Calculation assumes equilibrium mixture of Zr, Nb-95.

(c) Result is questionable..

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TABLE A-II - PART 1ANALYTICAL RESULTS FOR THE 4" CORE SAMPLE

<u>Measurement</u>	<u>Samples (a)</u>			
	<u>H₂O-1</u> 7.0g salt <u>μc/g</u>	<u>HCl-1</u> 1.8g salt <u>μc/g</u>	<u>H₂O-2</u> 4.9g salt <u>μc/g</u>	<u>HCl-2</u> 2.3g salt <u>μc/g</u>
<u>Direct γ Energy Analysis</u>				
Ru-103	33	249	53	213
Ru-106	238	1630	326	1090
Ce-141	(c)	(c)	(c)	(c)
Ce,Pr-144	617	1040	768	365
Zr-95 ^(b)	7.3	182	10.6	100
Cs-137	117	60	130	7.3
<u>Ruthenium Separation γ Counting</u>				
Ru-103	44	336		
Ru-106	177	1160		
<u>Strontium Separation</u>				
Sr-89	31	24		
Sr-90	82	66		
<u>Cerium Separation β Absorber Counting</u>				
Ce-141	27	30		
Ce,Pr-144	490	750		
<u>Cesium Separation, Cs-137</u>				
	122	68		
<u>Zirconium Separation, Zr-95</u>				
	6.8	66		

(a) Sample received 4-27-64. Analytical results corrected for radioactive decay to 4-29-64. Weight of salt is the amount of salt dissolved in the H₂O or HCl leach.

(b) Calculation assumes an equilibrium mixture of Zr,Nb-95.

(c) Not detectable.

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TABLE A-II - PART 2ANALYTICAL RESULTS FOR THE 4" CORE SAMPLE

<u>Measurement</u>	<u>Samples (a)</u>			
	<u>H₂O-3</u> 8.4g salt <u>μc/g</u>	<u>HCl-3</u> 0.7g salt <u>μc/g</u>	<u>H₂O-4</u> 27.7g salt <u>μc/g</u>	<u>HCl-4</u> 9.7g salt <u>μc/g</u>
<u>Direct γ Energy Analysis</u>				
Ru-103	48	1030	39	520
Ru-106	257	5290	201	2310
Ce-141	(c)	(c)	(c)	(c)
Ce, Pr-144	748	1890	2020	1200
Zr-95 ^(b)	5.7	491	0.67	101
Cs-137	112	40.6	166	47.8
<u>Ruthenium Separation γ Counting</u>				
Ru-103			53	624
Ru-106			134	1880
<u>Strontium Separation</u>				
Sr-89			19	17
Sr-90			59	106
<u>Cerium Separation β Absorber Counting</u>				
Ce-141			68	4
Ce, Pr-144			1690	936
<u>Cesium Separation, Cs-137</u>			171	54
<u>Zirconium Separation, Zr-95</u>			1.1	13.8

(a) Sample received 4-27-64. Analytical results corrected for radioactive decay to 4-29-64. Weight of salt is the amount of salt dissolved in the H₂O or HCl leach.

(b) Calculation assumes an equilibrium mixture of Zr, Nb-95.

(c) Not detectable.

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TABLE A-II - PART 3

ANALYTICAL RESULTS FOR THE 4" CORE SAMPLE

<u>Measurements</u>	(a)	
	<u>Samples</u>	
	<u>H₂O-HCL Leached Wool #4</u> <u>0.1512g dissolved</u> <u>µc/g</u>	<u>#4 Crust</u> <u>35.2mg dissolved</u> <u>µc/g</u>
<u>Direct γ Energy Analysis</u>		
Ru-103	192	78
Ru-106	1120	471
Ce-141	(c)	(c)
Ce,Pr-144	54	244
Zr-95 ^(b)	539	211
Cs-137	21	96
<u>Ruthenium Separation</u> <u>γ Counting</u>		
Ru-103	239	116
Ru-106	790	344
<u>Strontium Separations</u>		
Sr-89	1.8	47
Sr-90	23	122
<u>Cerium Separation</u> <u>β Absorber Counting</u>		
Ce-141	1.5	151
Ce-,Pr-144	33	1860
<u>Cesium Separation, Cs-137</u>	23	93
<u>Zirconium Separation, Zr-95</u>	568	205

- (a) Sample received 4-27-64. Analytical results corrected for radioactive decay to 4-29-64. Weight of salt is the amount of salt dissolved in the H₂O or HCL leach.
- (b) Calculation assumes equilibrium mixture of Zr,Nb-95.
- (c) Not detectable.

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APPENDIX BACCUMULATION MODEL

Under normal operating conditions it would be expected that solid materials and any associated fission product activity build up on the Purex canyon ventilation exhaust filter at rather uniform rate⁽⁴⁾. Samples of the filter should therefore contain a composite accumulation ranging downward in time of deposition from a maximum of about eight years, corresponding to plant start-up in 1956, to the time of sampling.

The fission product spectrum is characteristic of the duration and possibly the rate of deposition. A green or predominately short cooled fission product mixture is indicative of recent rapid accumulation, whereas a fission product spectrum consisting mostly of longer lived nuclides is typical of the normally expected long-term accumulation. Should activity accumulate on the filter in a sequential manner, for example from the top down, a fission product mixture age difference will be observed between sections of the filter.

Fission product ratio plots corresponding to constant rate accumulation were constructed from the data of Van Tuyl⁽²⁾ assuming irradiation and cooling parameters for the material suggested by⁽⁴⁾ as representative of plant dissolver solutions.

If freshly irradiated material is allowed to cool briefly and is then adsorbed at constant rate on a filter, the total number of curies of a particular fission product nuclide accumulated is given by the expression⁽³⁾

$$X_t = \frac{C_0 e^{-\lambda_x d}}{\lambda_x} (1 - e^{-\lambda_x t})$$

where X_t is the total curies accumulated per unit amount of material adsorbed per unit time, C_0 is the concentration of the nuclide at discharge in curies per unit amount of material, λ_x is the nuclide decay constant in days⁻¹, d is days cooling subsequent to discharge, and t is the accumulation interval in days.

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As the accumulation time t becomes very large $e^{-\lambda_x t}$ approaches zero and the number of curies of the nuclide adsorbed on the filter approaches a maximum value X_{Max} such that

$$\begin{aligned} X_{Max} &= \frac{C_0 e^{-\lambda_x d}}{\lambda_x} \\ \text{and} \\ X_t &= X_{Max} (1 - e^{-\lambda_x t}) \end{aligned}$$

The absolute amount of a particular nuclide adsorbed cannot be conveniently calculated because accumulation rate is difficult to evaluate. The ratio of amounts of two isotopes is independent of rate, however, and is equal to the ratio of the respective X_t values. Since all X_t values approach limits with increasing accumulation time, isotopic ratios approach constant value.

Plots of Sr-89/Sr-90, Zr-95/Cs-137, Ru-103/Ru-106, and Ce-141/Ce,Pr-144 isotopic ratio as a function of accumulation time at constant rate are presented in figures B.1, B.2, B.3, and B.4.

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FIGURE B.1

RUTHENIUM-103/RUTHENIUM-106 RATIOS AS A FUNCTION OF
BUILDUP DURATION

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Ce-141/CePr-144 Isotopic Ratio

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